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SULFUR IN THE CORROSION OF SUPERALLOYS

Final Report

for

The Period, 1 April 1974 through 30 June 1977

by

J. Bruce Wagner, Jr.

Materials Research Center and Department of Materials Science
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November 1977

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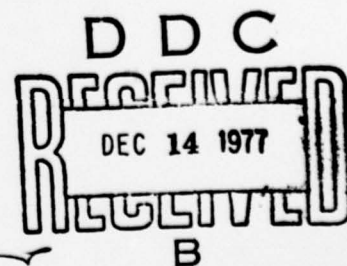
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Radiotracer sulfur-35 has been diffused into single crystals of nickel oxide as a function of oxygen pressure, doping additions of lithium or chromium and temperature (1000° to 1250°C). The measured data were found to deviate markedly from the error function complement dependence for diffusion from a constant source. The deviation is attributed to the migration of sulfur by the "double mode simultaneous diffusion mechanism." The faster mode is suggested to be via nickel vacancies and the slower mode via oxygen vacancies.		

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Abstract continued:

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The diffusivities are: $D(\text{fast}) = 2.94 \exp(-86.6 \text{ kcal/RT})$ and $D(\text{slow}) = 1.08 \times 10^{-9} \exp[-32.8 \text{ kcal/RT}]$. These data show that sulfur migrates through nickel oxide by two different mechanisms at two different rates. A concurrent study was performed on the SO_2 - O_2 corrosion of Ni and Ni-2 $\frac{1}{4}$ % Cr alloy between 900 and 1050°C. Constant oxygen pressure (20%) was used and 0, 2, 5 and 10% SO_2 with the balance argon. The rates of corrosion increased as the percent SO_2 increased, attaining an apparent maximum between 5 and 10%. No sulfides were found at the nickel-nickel oxide interface.

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10 to the -9th power

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List of manuscripts submitted or published under Army Research Office sponsorship during this period.

1. "The Diffusion of Sulfur-35 in NiO" by D. R. Chang, R. Nemoto and J. B. Wagner, Jr. Trans. Met. Soc. 7A, 803 (1976).
2. "Diffusion of Sulfur in Nickel Oxide Single Crystals," by W. Howng and J. B. Wagner, Jr. submitted to J. Phys. Chem. Solids, February 1977.
3. "The Oxidation of Pure Ni and a Ni-2 $\frac{1}{4}$ % Cr Alloy in Atmospheres Containing Sulfur Dioxide," Proc. of a Symposium on High Temperature Alloys, October 1976, The Electrochemical Society, Proc. Vol. 77-1 edited by Z. A. Foroulis and F. S. Pettit.
4. "Electrical Conductivity, Diffusion and Minority Defects in Some Transition Metal Oxides" by J. Bruce Wagner, Jr. in Defects and Transport in Oxides, edited by M. Seltzer and R. Jaffe, Plenum Press, N. Y. (1974) p. 283.

Scientific Personnel supported by this project and degrees awarded during this period:

1. Wei-Yean Howng, graduate student, 16 April 1974 through 1 January 1977.

Ph.D. degree awarded June 1977, Northwestern University.
Thesis title: "Sulfur Transport in Nickel Oxide."
2. Michael Stark, graduate student, 16 June 1975 through 30 April 1977.
3. Walter Wahnsiedler, postdoctoral research associate, 1 September 1974 through 30 September 1974.
4. J. van Ballegooijen, Visiting scholar, 1 August 1974 through 28 February 1975.

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FINAL REPORT

In some examples of hot corrosion, sulfide phases are found beneath the oxide scale near or at the metal scale interface. The mechanism of transport of sulfur through these scales is of immediate practical interest and also of theoretical interest for a general understanding of transport of anions through oxides. Accordingly, studies of the diffusion of sulfur-35 (a weak beta emitter) have been carried out on single crystalline NiO.

Undoped single crystals and crystals doped with lithium or chromium were grown by the Vernueil flame fusion method at Northwestern University. Rectangular parallelopipeds approximately 4 x 4 x 1.5 mm were cut with (001) faces. These were given a pre-anneal in about one atmosphere of oxygen inside a quartz ampoule to fix Ni / O ratio. The samples were quenched and radio tracer sulfur-35 dissolved in benzene was applied to one crystal face of the sample. The benzene was evaporated leaving the radio tracer. The sample was again sealed in a quartz tube then given a diffusion anneal at the same oxygen pressure and temperature as the prediffusion anneal. The sample was quenched and the residual activity counted as successive layers were ground off.

The results showed the penetration profiles did not obey the simple error function complement for a constant source into a semi-infinite sink. Instead the penetration profiles could be fitted to the superposition of two complementary error functions corresponding to the diffusion of two

independently migrating species. One of these diffused faster than the other.

The results were

and D (fast mode, S-35 in NiO) = $2.94 \exp\left[\frac{86.6 \text{ kcal/mole}}{RT}\right] \text{ cm}^2/\text{sec}$

D (slow mode, S-35 in NiO) = $1.08 \times 10^{-9} \exp\left[\frac{-32.8 \text{ kcal/mole}}{RT}\right] \text{ cm}^2/\text{sec}$

for an oxygen pressure of approximately one atmosphere.

Additions of chromium, a donor, to NiO, increased the diffusivity of the fast mode and decreased that of the slow mode. Additions of lithium, an acceptor, effected just the opposite behavior. Moreover, the diffusivity of the fast mode decreased as the oxygen pressure decreased and conversely for the slow mode. These data suggest that the slow mode represents diffusion of sulfur via anion vacancies as was previously reported (1). The faster mode is inferred to diffuse via cation vacancies inasmuch as the addition of chromium increases this mode and the addition of lithium decreases it.

In a parallel study (2), the corrosion of nickel and a nickel-2-1/4 w/o Cr alloy were studied in atmospheres containing SO₂. Temperatures of 900 - 1050°C were used and the initial gas compositions were

<u>% O₂</u>	<u>% SO₂</u>	<u>% Argon</u>
20	0	80
20	2	78
20	5	75
20	10	70

The oxidation of unalloyed Ni in 20% O₂ - 80% Argon obeyed parabolic kinetics and rate constants were in agreement with previous literature values (3,4). The oxidation kinetics for the Ni - 2-1/4 w/o Cr alloy were more rapid than the unalloyed Ni owing to the doping effect of the chromium in the NiO scale. The addition of SO₂ to the gas mixtures increased the rates for the 2% and 5% SO₂ mixtures. The rates in the 10% SO₂ mixture decreased from that at 5% SO₂ for both the unalloyed nickel and the nickel-chromium alloy. Representative samples were cross sectioned and examined metallographically and by scanning electron microscopy. The unalloyed nickel samples exhibited no sulfide phase at the scale-metal interface. This phenomenon was unexpected since previous studies in the same laboratory by Chang (5) had shown the presence of sulfides at the scale-metal interface. Differences in the initial surface polish were noted and a series of tests were carried out to determine whether surface pretreatment could affect the presence or absence of sulfides at the scale-metal interface. Unalloyed nickel was given an electropolish and then oxidized at 1060°C as follows:

- a) Pre-oxidized 14 hours in 20% O₂ - 80% Argon followed by
100 hours in 20% O₂ - 70% Argon - 10% SO₂
- b) 100 hours in 20% O₂ - 70% - 10% SO₂ without preoxidation.

Samples were fractured to avoid removal of sulfides by the mechanical polishing technique. The samples were examined in the SEM and traverses using the X-ray dispersive analyzer were carried out. No sulfide phase was detected at the metal-scale interface for either sample. Furthermore, the

sample B exhibited large columnar grains and virtually no visible porosity. These scales contrasted with those formed previously (5) in which the scales exhibited a large fraction of porosity and there was a sulfide phase at the metal-scale interface. The difference in behavior was attributed to the difference in the presence of pores. Furthermore, the diffusion of sulfur by bulk diffusion is too slow to penetrate the growing scale unless migration via pores or boundaries is possible. These results indicate the importance of initial surface finish on hot corrosion of metals. Further studies are underway to test this working hypothesis further.

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